Molecular Crystallization Controlled by pH Regulates Mesoscopic Membrane Morphology

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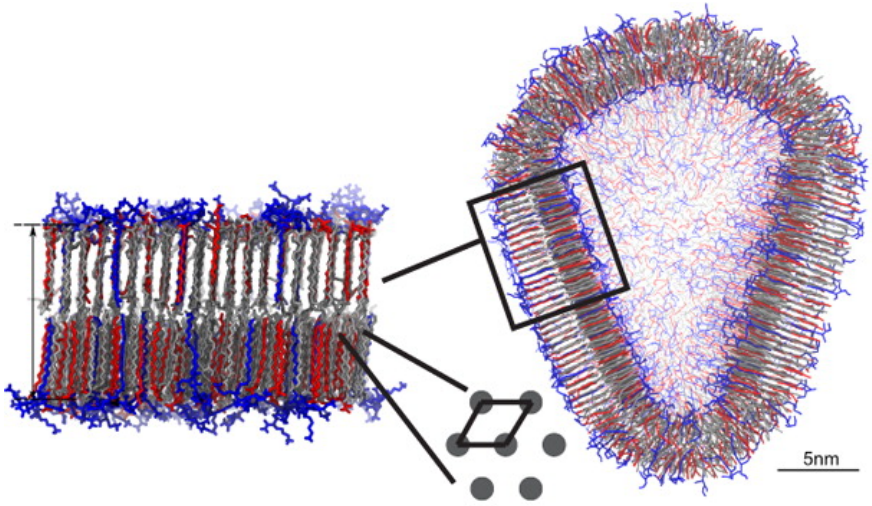
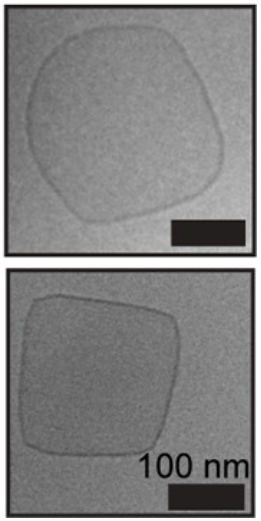
By co-assembling oppositely charged lipids with variable degrees of ionization, we found a mechanism that leads to complex crystalline polyhedral shells and showed how their crystalline structures can be modified by externally modifying the surrounding electrolyte. That is, we found a way to regulate the shape of crystalline nano-containers. The buckled diverse geometries include fully faceted regular and irregular polyhedral, such as square and triangular shapes, or mixed Janus-like vesicles with faceted and curved domains that resemble cellular shapes and wall envelops of halophilic organisms.





The symmetries of the resulting ionic nanocontainers were regulated by the pH values of the solution, which induced changes in their molecular structures. Transmission electron microscopy and in situ small- and wide- angle X-ray scattering demonstrated that these faceted ionic shells have hexagonal crystalline symmetry and that this symmetry makes them stable in closed shapes, and at high salt concentrations. Atomistic simulations revealed that the competition of physical interactions and charge-regulation induced transitions in crystalline states that translate in changes of shapes. The changes in packing symmetry translate in bilayer thickness changes that open the closed shapes (like a switch). The atomistic simulations demonstrated that the bilayer thickness and molecular packing are not homogeneous in the low symmetry closed shapes. The curved regions are less ordered and therefore would allow higher transport of molecules than the crystalline flat polyhedra faces. These discoveries shed light in the function of polyhedral cellular shells. Moreover, understanding the coupling of shape and composition through tuning chemical and physical interactions will enable the design of polyhedral structures for various applications including efficient nano-reactors to perform specific catalytic functions.

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